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EXPANSION AND COMPRESSIBILITY OF ETHER AND OF ALCOHOL IN THE NEIGHBORHOOD OF THEIR BOILING POINTS.

BY ALPHEUS W. SMITH.

Presented by E. H. Hall, May 9, 1906. Received October 30, 1906.

[For a summary of the results reached in this paper, see p. 458.]

INTRODUCTION.

THIS subject was suggested to the writer by Professor Hall, to whom it became of interest in his work on the van der Waals a in ethyl ether and in ethyl alcohol. In obtaining values of the van der Waals a by one of the methods employed in that paper[1] Professor Hall found it desirable to know both the coefficient of expansion and the coefficient of compressibility of these liquids just before they change into the vapor state.

The investigators who have concerned themselves with the coefficients of expansion and of compressibility of liquids have for the most part used large differences of temperature and of pressure in producing the change of volume in the liquid, so that every coefficient is the average coefficient over a considerable range of temperature and of pressure. Such data do not give us with certainty the coefficient of expansion and of compressibility at a particular temperature and at a pressure differing but little from the vapor pressure of the liquid at that temperature.

I, therefore, undertook to find by means of new measurements both the coefficient of expansion and the coefficient of compressibility of the two liquids in question at pressures which were only slightly greater and at those which were somewhat less than the vapor pressure of the liquid at the temperature used, — i. e., the coefficient of expansion and the coefficient of compressibility of these liquids just before they reach their boiling conditions, and these same coefficients when the liquids are in the superheated state.

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[1] Boltzmann-Festschrift. 1904.

If T is the absolute temperature, p the external pressure, v the specific volume, k the coefficient of compressibility at constant temperature, and e the coefficient of expansion at constant pressure, then k and e have by definition the following meanings.

$$k = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right),$$

$$e = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right).$$

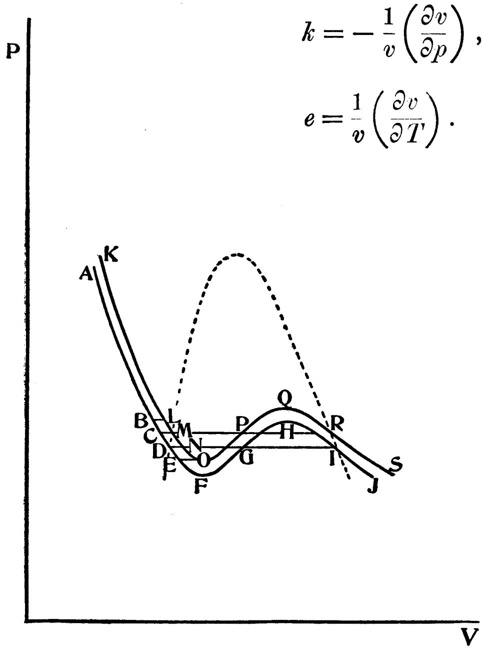

Figure 1.

If, according to the van der Waals equation, we plot on the pv-plane, as in Figure 1, the isothermals of the liquid, k and e each have a geometric interpretation ; k is the reciprocal of the slope of the isothermal divided by v; and e is the distance between two isothermals measured parallel to the v-axis, divided by the difference of temperature between the isothermals and divided also by v.

The purpose of this research may now be made somewhat clearer by an examination of Figure 1, where we will suppose that we have plotted two of the isothermals of either ethyl ether or ethyl alcohol. Suppose the temperatures for which these isothermals are plotted differ from each other only by two or three degrees. To be specific, consider the isothermal A F H J. On this isothermal the point D represents the liquid when it is under a pressure equal to its vapor-pressure. The part D F of this isothermal represents the liquid in the superheated state. We are to determine the slope of such an isothermal, (1) at B and C, where the external pressure exceeds the vapor-pressure by about one atmosphere, (2) at D, where the external pressure is equal to the vapor-pressure, (3) at E, where the external pressure is less than the vapor-pressure. Furthermore, the distance B L between any two neighboring isothermals, when p is equal to one atmosphere, is to be compared, (1) with the distance C M between the same isothermals when p is equal to the vapor-pressure of the liquid at the higher temperature, (2) with the distance E O between these isothermals when p is less than the vapor-pressure of the liquid at either of the temperatures. B L, C M, and E O are parallel to each other and to the v-axis.

PART I: LIQUIDS UNDER PRESSURES GREATER THAN THEIR VAPOR-PRESSURES.

Thermostat.

In order to study the compressibility of liquids at low pressures, one must use small differences of pressure, not greater than 10 or 15 cm. of mercury, in getting the change of volume in the liquid. The changes in volume which result from such slight changes of pressure are very small and, since the coefficient of expansion of each of these liquids is large in comparison with its coefficient of compressibility, small changes in the temperature would introduce large errors in the determination of the compressibility. So small a change of temperature as 0.001° C., in either of these liquids, would introduce an error of about 3.5 per cent in the compressibility, if the change of volume were produced by increasing or by decreasing the pressure 20 cm. of mercury. If, therefore, the data were to have an accuracy of one per cent, the constancy of the temperature would become an important question. Moreover, the apparatus to be introduced into the thermostat was of such a form that the ordinary types of thermostats did not lend themselves to the purposes of this experiment. After some difficulty the following type was devised, which has met very well the requirements of this experiment.

The thermostat consisted in the main of a rectangular box, which was 150 cm. long, 60 cm. high, and 46 cm. wide. This box for brevity will be referred to as the *air-bath.* The top of the air-bath could be removed at will to allow the introduction of apparatus. Extending the whole length of the air-bath at mid-height of each side was an opening 2 cm. in width. These openings were covered with plate glass and served as windows through which observations could be made in a manner to be described later. In the interior of the air-bath, along its sides and bottom at a distance of about 5 cm. from the adjacent walls, were strung spirals of No. 18 german-silver wire, which in the aggregate had a resistance of about 20 ohms. These coils of wire, when connected in series with the city alternating circuit of 110 volts, served as heating coils by means of which the temperature of the air-bath could be raised to any desired value less than 60° C. In order to keep the air in the air-bath homogeneous as to temperature, a fan-motor which ran at fairly constant speed was placed at each of its ends. These motors stood just outside of the air-bath, and their shafts, each carrying a fan, projected into the interior.

For the regulation of the temperature of the air in the air-bath a modified form of the usual device, depending upon the expansion of alcohol, was used. A brass tube, with thin walls and an internal diameter of about 0.7 cm., was wound in the form of a spiral 50 cm. long and 6 cm. in diameter. One end being closed, the other was connected by means of a short piece of stout rubber tubing to the larger end of the glass tube, GADB (Figure 2). It was found better to make the spiral of brass than of glass. The brass, having a lower specific heat and a higher thermal conductivity than the glass, allowed the liquid which it contained to assume more rapidly the temperature of the air which surrounded it. The large surface which the spiral presented, in comparison with the volume of liquid which it contained, about 150 (cm.)^3, increased the rapidity with which the liquid assumed the temperature of the surrounding air. The spiral stood in a vertical position in the air-bath, and the glass tube B D (Figure 2) was also vertical. The thermo-regulator was filled with well-boiled alcohol. From the line E F around to the platinum point at B, it contained mercury. By taking out, or by adding mercury or alcohol, one fixed the temperature of the air-bath at any desired value. The platinum wires A and B (Figure 2) were con-

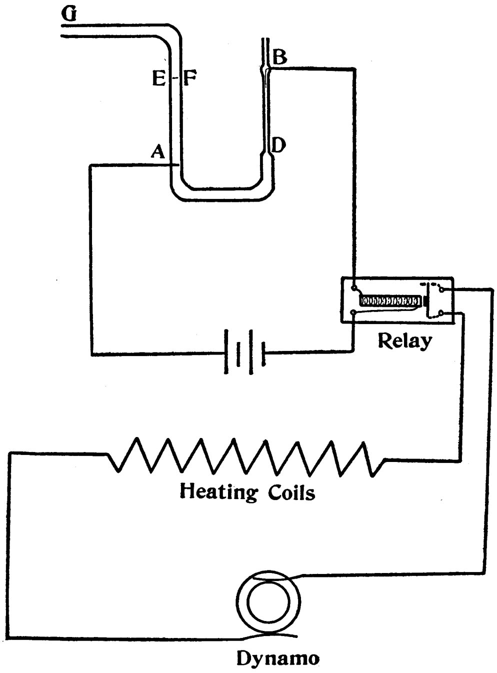

FIGURE 2.

nected in series with a relay of 1700 ohms and a battery of 8 volts. The other terminals of the relay were connected in series with the heating coils of the air-bath. These connections are shown diagrammatically in Figure 2. The oscillations which occurred in the air-bath were of the order of 0.2° C., and took place in about one minute.

I thought it well to isolate a portion of the space inside of the air-bath from the remainder by means of non-conducting materials, hoping thus to get an inner region in which these oscillations of temperature would have little effect. Since the apparatus to be kept at constant temperature was about 70 cm. long, and was to lie in a horizontal position, I chose as the region to be thus isolated the space inside of a cylindrical shell, 120 cm. in length, 15 cm. in internal and 25 cm. in external diameter. The walls of this cylindrical shell were made of concentric sheets of asbestos, the space between these sheets being packed with asbestos wool. The openings in the ends were filled with cotton wool. For the purposes of observation, it was necessary to have two narrow windows in the shell. These windows were diametrically opposite each other, and the glass plates closing them were at the inner surface of the shell. The temperature of the space thus enclosed was found to remain very nearly constant.

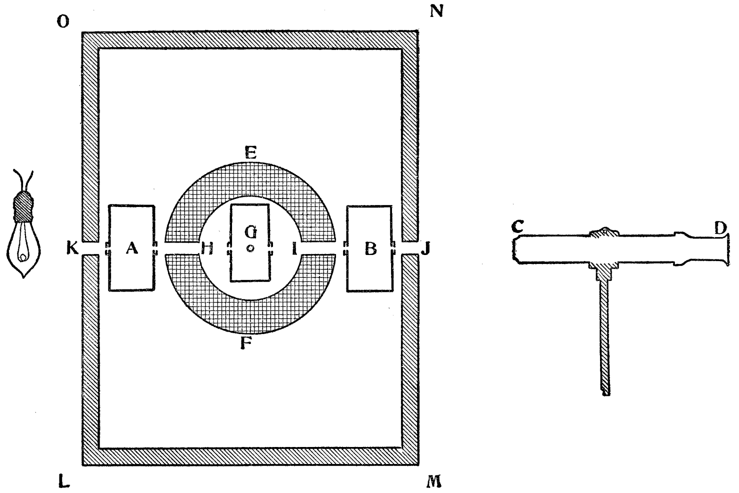

FIGURE 3.

An incandescent lamp was used as a source of illumination, and at first the heat from it, passing into the thermostat, caused a slight drift of temperature. To prevent this drift, and to prevent, as far as possible, the flow of heat from the thermostat into the room, water-windows were placed just inside of the air-bath and opposite the small openings in the cylindrical shell.

Figure 3 shows a cross section of the thermostat, made through the water-windows, the telescope, and the source of illumination. L M N O is the air-bath; E and F are the halves of the cylindrical asbestos shell; A and B, the two water-window s. The openings at K and J and those at H and I, were closed by plate-glass windows.

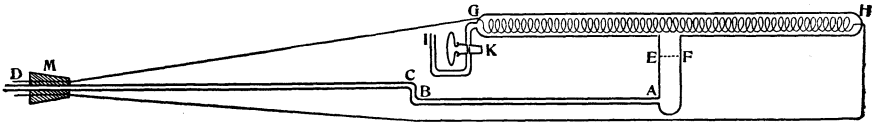

FIGURE 4.

Dilatometer and Piezometer.

The dilatometer (Figure 4) consisted of a cylindrical glass bulb H G, 30 cm. long and 1.7 cm. in diameter. For purposes of filling, which operation will be described later, one end of this bulb was closed by means of the stopcock K. At right angles to the axis of the bulb and midway between its ends was sealed another glass tube 5 cm. long, and of the same internal diameter as the bulb. The lower end of this short tube was closed, and to it was sealed the capillary tube A B C D, which from A to B was parallel to the bulb, from B to C at right angles to it, and from C to D again parallel to it. Near the end D this tube carried the rubber stopper M. The purpose of this stopper will be explained later. Inside the bulb of the dilatometer there was a spiral of fine platinum wire, to be used as a platinum thermometer. The description of the use of this platinum thermometer will be postponed.

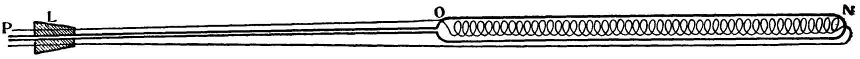

FIGURE 5.

The piezometer (Figure 5) consisted of the cylindrical bulb O N, to one end of which was sealed the capillary tube O P. The piezometer also contained a platinum thermometer, the lead wires of which passed out through the rubber stopper L. The capacity of the piezometer was determined by weighing it empty and then weighing it filled with distilled water at a known temperature. The capacity of the dilatometer was determined in precisely the same way. The former had a capacity of 64.04 $(\text{cm.})^3$, the latter a capacity of 70.32 $(\text{cm.})^3$.

The capillary stem of the piezometer, and also that of the dilatometer, was calibrated by use of a mercury column, so that the cross section of each of them was accurately known at all points. The capillary tube of the dilatometer, which had a mean cross section of 0.01918 $(\text{cm.})^2$, happened to have a very uniform bore, which showed a variation of only about one half of one per cent over a distance of 20 cm. The capillary tube of the piezometer, with a mean cross section of 0.01536 $(\text{cm.})^2$, showed a variation of about 2 per cent over a distance of 20 cm.

Brass Jacket.

In order to have the pressure on the inside of the piezometer the same as that on its outside it was inserted in a rectangular brass vessel which for the sake of brevity will be referred to as the *brass jacket*. In the course of the whole work two slightly different types of brass jackets were used. As their differences were of minor importance, only one of them will be described. The brass jacket consisted essentially of a rectangular brass box 71 cm. long, 11 cm. high, and 5 cm. wide, the walls of which were made of strips of brass 0.6 cm. in thickness. In one end of the brass jacket there was a rectangular opening 7 cm. long and 3 cm. wide, through which the piezometer or dilatometer could be introduced. This opening was then closed by the means of two castings, which were separated from each other and from the end of the brass jacket by means of rubber gaskets. These castings, after being firmly joined together and to the end of the brass jacket by means of screws, afforded a conical shaped orifice into which M (Figure 4) or L (Figure 5) fitted snugly. In order to prevent the stopper from coming out under pressure greater than one atmosphere, it was pressed into the conical orifice by means of a disc which, having at its centre an aperture through which passed the capillary stem of the piezometer or the dilatometer and the lead wires of the platinum thermometer, was firmly fastened to the castings by means of four screws. In either side of the brass jacket was a narrow window, closed by thick plate glass used with a rubber gasket, through which observations could be made. Into the top of the brass jacket and near each of its ends was inserted a short cylindrical brass tube. One of these tubes was connected to the pressure gauge so as to allow any desired pressure to be applied to the liquid in the brass jacket. The other was for purposes of filling, and was closed with a cylindrical brass cap after the filling.

Although the brass jacket was designed especially for experiments on compressibility, it was found convenient to insert the dilatometer in it. Figure 6 shows the brass jacket with the dilatometer in position. Part of one side is removed to show the dilatometer in the interior.

Pressure Gauge.

For the measurement of the pressure on the liquid an open manometer of the form shown in Figure 7 was used. In this figure parts of the vertical tubes are omitted. The manometer was made of heavy glass tubing with an internal diameter of 1.2 cm. The U-shaped part of the tube was filled with clean mercury to a height of 120 cm. Between the branches A B and C D of the U-shaped part of the tube were placed meter rods, end to end, on which one read off the difference in height of the mercury in the two parts of the tube. One had, of course, to read the barometer each time in order to get the absolute pressure on the liquid. From H and G the pressure gauge was connected by means of pressure tubing to the capillary tube of the piezometer or the dilatometer and to the small tube in the top of the brass jacket. Hence the internal and the external pressure on the walls of the piezometer or of the dilatometer were the same. By means of the stopcock K_1 the pressure gauge could be made to communicate with the external atmosphere. The large tube I, which was 42 cm. long and 5.5 cm. in diameter, served as an air-chamber into which air could be forced or from which it could be exhausted. By turning the stopcock K_2 the pressure on the liquid could be increased or decreased by as small an amount as one wished. The other end of I was closed with the stopcock K_3.

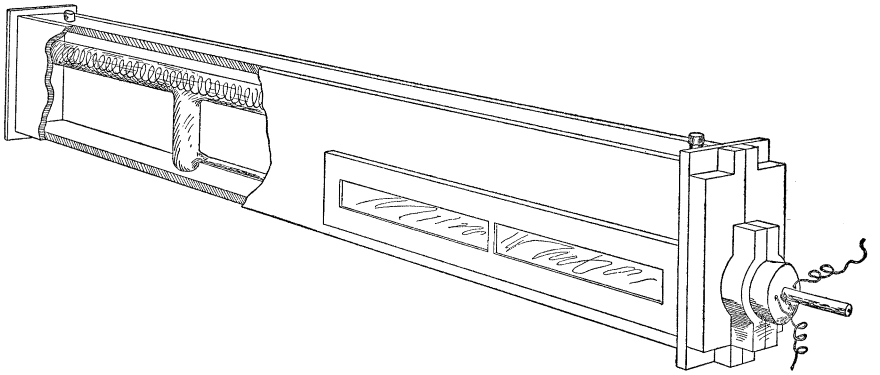

FIGURE 6.

The stopcock K_4 was for convenience in case the mercury had for any reason to be removed from the pressure gauge.

Filling the Dilatometer and the Piezometer.

The greater part of the capillary stem and the short vertical tube of the dilatometer up to the line E F (Figure 4) were filled with a known amount of clean, dry mercury. The mercury was poured into the dilatometer, care being taken to avoid, as far as possible, any air bubbles. One, however, could never be perfectly sure that slight traces of air were not left either in the mercury or along the sides of the tube which contained the mercury. Since the coefficient of expansion of air is only about twice the coefficient of expansion of either ethyl ether or of ethyl alcohol, these very slight traces of air would introduce no appreciable error in the data on the expansion of these liquids. The end of the capillary tube being closed, I (Figure 4) was joined by means of a short piece of rubber tubing to a glass tube bent so as to dip into a flask containing the liquid to be investigated. This liquid had been previously boiled to remove traces of air. By alternately heating the dilatometer above the boiling point of the liquid and then cooling it, the bulb of the dilatometer was finally filled with liquid which was free from air. When the liquid had assumed a temperature nearly equal to the temperature at which observations were to be made, the stopcock K was closed.

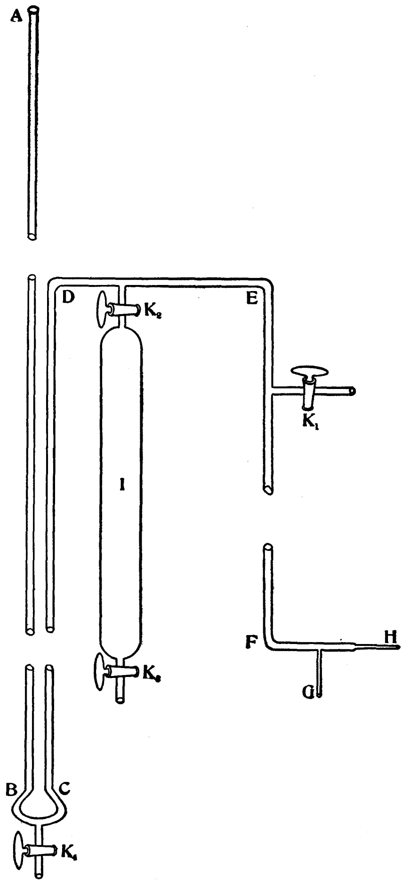

FIGURE 7.

It was desirable to have the mercury in the dilatometer for two reasons. At low pressures the otherwise free surface of the ether or the alcohol in the capillary tube afforded an opportunity for evaporation, and as considerable time elapsed between observations on the coefficient of expansion, the loss due to evaporation would introduce some error in the measurement of the change of volume. Furthermore, the liquid retreating down the capillary tube with decreasing temperature, leaves a film on the walls of the tube. This makes the observed change of volume greater than the true change of volume. This film will not disappear for a long time, and a similar cause of error enters when the temperature is again increased. Both of these sources of error were avoided by having mercury in the lower part of the dilatometer.

It was hoped that a piezometer of the same form as the dilatometer might be used in the work on compressibility; for the error due to the adhesion of the liquid on the walls of the capillary tube enters into the data on compressibility as it did into the data on expansion. The error due to the evaporation from the surface of the liquid was in the work on compressibility not large enough to be of importance; for the observations on compressibility were made very rapidly. It was, however, found that since it was impracticable to boil the mercury into such a piezometer, the slight traces of air from which the bulb and stem could not be entirely free, introduced serious error in the compressibility at low pressures. It was therefore decided to dispense with the mercury in the piezometer, and to use an instrument of the kind shown in Figure 5. The liquid was boiled into this piezometer in the same way in which it was boiled into the dilatometer. After the filling, the liquid in the bulb was heated 2° or 3° C. above the temperature at which observations were to be made. When the liquid again cooled down to the desired temperature, the exposed surface was somewhere near the middle of the capillary tube O P.

It was possible to get a rough estimate of the error due to the adhesion of the liquid on the walls of the tube. A glass tube of about the same bore as the capillary tube of the piezometer was filled with ether or alcohol and the liquid was then allowed to flow out of it, leaving the inner walls of the tube wet. The weight of the film of liquid adhering to the tube was determined at once. Knowing the capacity of the tube, one found that about 2.5 per cent of the liquid was left on the walls of the tube. In all the work on compressibility the necessary correction was made for this source of error.

Measurement of Change of Volume.

Since the cross section of the capillary tube of the piezometer and that of the dilatometer were accurately known, in order to measure the change of volume corresponding to a definite change of pressure or of temperature one need only observe the distance which the liquid meniscus in the capillary tube moved. For this purpose a telescope mounted with its axis horizontal on the screw of a dividing-engine was used. The position of the telescope of the dividing-engine is indicated in Figure 3. The screw of the dividing-engine had a pitch of 0.05 cm. and was graduated to read to 0.000125 cm.

Measurement of Temperature.

It has been already pointed out that both the piezometer and the dilatometer contained a platinum thermometer for the measurement of the temperature of the liquids. Both of these thermometers were taken from the same piece of fine platinum wire, which was about 0.015 cm. in diameter. This wire was in each case annealed by passing through it a current of 2 amperes for about 6 seconds. The wire was then wound in the form of a helix, 30 cm. long and 1.3 cm. in diameter. To each end of the helix was hard-soldered a short piece of rather stout platinum wire. This was found necessary in order to prevent the wire from breaking off where it was sealed into the ends of the glass bulbs, G and H (Figure 4) and O and N (Figure 5). Each of the platinum spirals, when inside the bulb, extended nearly the whole length of the bulb, and the axis of the spiral coincided nearly with the axis of the bulb. To the terminals of the spirals were soldered copper lead wires, which, after being carried along parallel to the capillary tubes of the dilatometer and the piezometer respectively, passed out through the respective rubber stoppers M (Figure 4) and L (Figure 5). It was found necessary to enclose these lead wires in fine rubber tubing, in order to prevent battery-action between them and the liquid in which they were subsequently immersed. The total resistance of the lead wires on the dilatometer was 0.114 ohm, while those on the piezometer had a resistance of 0.123 ohm.

Since both platinum thermometers were taken from the same piece of wire and had been treated in precisely the same way, it seemed sufficient to calibrate only one of them. I calibrated the platinum thermometer which was in the piezometer and used the temperature coefficient thus obtained in the work with the one which was in the dilatometer. In the calibration of the platinum thermometer the bulb of the piezometer was immersed in a mixture of ice and water or in the vapor of one of the following liquids, boiling under atmospheric pressure, — water, benzol, chloroform, and carbon disulphide. The temperatures, except those of melting ice and boiling water, were determined by means of a well-tested Baudin thermometer.

Table I shows the resistance of this platinum thermometer at the five temperatures previously referred to, and the change per degree of its resistance over the four intervals of temperature.

TABLE I.

$t°$ C.	Resistance.	Range of Temp.	Change per Degree.
0°	25.581 ohms		
		0 - 45.9	.0838 ohms
45°.9	29.432 "		
		45.9- 60.4	.0841 "
60°.4	30.640 "		
		60.4- 80.3	.0844 "
80°.25	32.323 "		
		80.3-100.2	.0895 "
100°.2	34.111 "		

It will be observed from this table that between 0° C. and 80° C. the change per degree in the resistance of the platinum wire is very nearly constant, and over this range of temperature shows a variation of about 0.7 per cent. Between 80° C. and 100° C. it increases about 1.2 per cent. As all the temperatures at which the platinum thermometer was used were below 80° C. the temperature of the liquid is obtained with sufficient accuracy from a knowledge of the change in the resistance of the platinum thermometer.

An attempt was made to fit the data into the formula of Callendar and Griffiths.[2]

$$T - pt = \delta\left[\left(\frac{T}{100}\right)^2 - \frac{T}{100}\right]$$

where

T = absolute temperature,

δ = constant,

$$pt = \frac{(R_t - R_0)\,100}{R_{100} - R_0}.$$

R_0 = Resistance of thermometer at 0° C.

R_t = " " " " t° C.

R_{100} = " " " " 100° C.

This attempt was, however, unsuccessful, and it appears that the law given by Callendar and Griffiths does not hold for the specimen of platinum wire here used.

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[2] Phil. Trans., **182**, A. (1892), p. 119.

The resistance at 0° C. of the platinum thermometer which was in the dilatometer was found to be 24.528 ohms.

For the measurement of the change in the resistance of the platinum thermometer during the experiments on compression and expansion a Carey-Foster bridge was used. The bridge wire, which was of manganin, was calibrated in the usual way and had a resistance of 0.01317 ohm per cm. The platinum thermometer was connected to the bridge by means of manganin lead wires with a resistance of 2.359 ohms and a temperature coefficient of 0.000015 per degree C. The coils on the other side of the bridge were also made of manganin wire, which had the same temperature coefficient as the lead wires. The resistance of each of these coils was accurately known. The change in the resistance of these coils due to change in their temperature was very small, but as it introduced in the coefficient of expansion an error of about 0.2 per cent for a change of 1° C., the temperature of the room in the neighborhood of the coils was always noted and the necessary correction applied. The temperature of the room never changed more than 2° C. or 3° C. between observations on expansion.

For a battery one Leclanché cell was used. A sensitive form of Thomson galvanometer was found satisfactory for the resistance measurements.

The heating of the platinum thermometer by the current used in measuring its resistance had, of course, to be considered. By putting a resistance of 1 ohm in the battery circuit and by using coils with a resistance of 0.1 ohm for balancing coils in the Carey-Foster bridge, it was practicable to reduce the current through the platinum thermometer to about 0.005 ampere. This current flowed for not more than one second. The amount of heat thus generated was small, and would, it seems, for the most part be communicated to the liquid which surrounded the platinum wire. Moreover, as this heating effect was always about the same, it could not at worst introduce more than a small constant error in the determination of the temperature, and in getting the change of temperature this small error would be eliminated. It may therefore be neglected here.

This method of measuring the change of temperature in the liquid was found quite satisfactory. In the work on expansion the temperature of the liquid was changed only 2° C. or 3° C. The corresponding change in the resistance of the platinum thermometer was never greater than the resistance of the bridge wire, and care was taken to measure the change of resistance in terms of the bridge wire alone. The work was thus free from any error that might have been made in determining the resistance of the standard coils. It was practicable to determine the change in the temperature of the liquid with certainty to 0.01° C., but the absolute temperature of the liquid was not known closer than 0.1° C.

Compressibility of Glass.

Since the liquid under examination was enclosed in a glass bulb which changed its capacity with change of pressure on the liquid, the change of volume in the liquid was partly hidden. As the piezometer contained a platinum thermometer, the compressibility of the glass of which it was made could not be determined directly in the usual way, by use of mercury. Accordingly another piezometer was made which differed from the first only in this, — that it contained no platinum thermometer. Its bulb was made from the same piece of glass tube from which the bulb of the other piezometer was taken. Its capillary stem had a mean cross section of 0.00541 $(\text{cm.})^2$ and had been calibrated in the usual way. The capacity of this piezometer, determined by weighing it empty and then weighing it filled with mercury, was found to be 63.21 $(\text{cm.})^3$. The mercury being at 20° C., observations were made in the usual way on the apparent change of volume of the mercury in glass for a change of pressure, external and internal, of three atmospheres. Before the measurement of the change of volume a wait of ten minutes was allowed for the heat of compression to disappear. Experiment showed, $k_1 - k_2 = 1.77 \times 10^{-6}$, where

k_1 = compressibility of mercury at 20° C.
k_2 = " " glass " " "

This value is the mean of twenty observations, — ten made by increasing and ten by decreasing the pressure. According to Amagat[3] $k_1 = 3.92 \times 10^{-6}$, whence $k_2 = 2.15 \times 10^{-6}$. This value is in good agreement with the value given by Amagat[4] and with that given by Richards and Stull.[5]

Expansion of Glass.

Not only does the capacity of the piezometer change when the pressure on it is changed, but also the capacity of the dilatometer changes when its temperature is increased or decreased. One must therefore know the coefficient of expansion of glass in order to make the necessary correction in the work on expansion of liquids. By the ordinary method with mercury, the coefficient of expansion of the glass in the dilatometer was found to be 0.00023. One cannot be sure about the last figure in this value, but an error of two or three units in that place is not of importance in the present work.

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[3] Comp. Rend., **108**, 228 (1889).
[4] Loc. cit.
[5] Publication No. 7 of Carnegie Institution of Washington.

Preparation of Liquids.

The ether used in these experiments was obtained from Kahlbaum and had been distilled over sodium. Not all the observations were made on the same specimen of ether, but they were all made on ether which had been treated in precisely the same way. The alcohol was purified in the usual way by distillation in the presence of lime. The distillation took place behind suitable drying tubes to prevent the alcohol from taking up water from the air, and during all subsequent work the flask containing the alcohol was not allowed to communicate with the external atmosphere except through a drying tube. The purity of the alcohol was determined by the ordinary methods of specific gravity. The purity corresponding to a particular density was found from the tables of Landolt and Börnstein.

Expansion.

After the dilatometer had been filled with liquid in the manner already described and had been placed in the thermostat and allowed to assume a constant temperature, the pressure on the liquid was fixed at the desired value and observations were made in the usual way on the change of volume corresponding to a change of 2° C. or 3° C. in the temperature of the liquid. Before the change of volume, or the change of temperature, was finally observed, about seven hours was allowed for the temperature to equalize. Sometimes the observations were made by increasing, and sometimes by decreasing, the temperature. The change of volume due to a change of 2° C. in the temperature of the liquid was rather large, causing a movement of about 15 cm. along the capillary stem, and no difficulty was experienced in measuring it. The observed change of volume due to a certain change of temperature was, of course, due to the change of volume of the liquid and of the mercury and of the glass bulb. Knowing the volume of the mercury in the dilatometer and its coefficient of expansion, one gets at once the change of volume due to this source. The error due to the expansion of the glass bulb was corrected for in the way already pointed out.

Tables II and III show the results of these observations. In these tables p is external pressure on the liquid, t_1 is the initial temperature, and t_2 is the final temperature; P is the vapor-pressure of the liquid at the corresponding temperature t_2. The values of the vapor-pressure at the different temperatures were obtained from vapor-pressure curves plotted from the data of Ramsay and Young,[6] and of Regnault.[7] The mean of the two values thus obtained is given in the first column of these tables. The values of the vapor-pressure given are certainly correct to within a few millimeters of mercury, an accuracy which is quite sufficient for our present purposes. Both the vapor-pressure and the external pressure are expressed in centimeters of mercury.

TABLE II.

EXPANSION OF ETHYL ETHER.

P.	p.	t_1.	t_2.	Δt.	$e \times 10^5$.	Mean $e \times 10^5$.
	73.5	22.1°	24.6°	2.45°	169	
	73.3	22.4	24.7	2.34	170	170
	51.5	22.3	24.7	2.40	170	
51.0	51.5	22.1	24.2	2.07	170	170
	73.5	26.5	28.8	2.29	172	
	73.4	26.3	28.7	2.42	171	
	73.3	26.4	28.7	2.29	172	172
59.0	59.3	25.9	28.3	2.35	171	171
	116.6	30.3	32.9	2.63	173	173
	73.2	30.1	33.5	3.41	175	
	73.3	30.5	33.5	2.99	176	
	73.5	30.2	32.8	2.62	174	
	73.4	30.5	33.0	2.51	173	
	73.5	30.7	33.3	2.61	173	174
	69.5	30.4	33.0	2.61	174	
69.0	69.5	29.8	32.6	2.81	174	174

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[6] Phil. Trans., **177**, I, 123 (1886).

[7] Mém. de l'Acad., **26**, 336 (1862).

TABLE III.

Expansion of Ethyl Alcohol — 99.5 Per Cent.

P.	p.	t_1.	t_2.	Δt.	$e \times 10^5$.	Mean $e \times 10^5$.
	73.5	20°.2	23°.5	3°.27	112	
	73.5	20.2	24.0	3.79	112	112
	6.5	20.4	24.3	3.89	111	
5.3	6.2	20.5	23.6	3.14	112	112
	74.2	39.0	42.4	3.39	115	
	74.1	39.4	42.9	3.52	116	116
	16.9	39.1	42.9	3.84	114	
16.0	17.0	39.6	43.5	3.92	116	115
	123.0	74.6	84.8	10.2	144	
	123.0	73.5	84.8	11.3	142	
99.0	123.0	73.5	84.4	10.9	142	143

Compressibility.

In compression the liquid is heated. One must therefore proceed in one of two ways. One must either wait for the heat of compression to disappear, or read the change of volume at once and correct for the error due to the heat of compression. The first method depends upon the operation being as nearly as possible isothermal; the latter, on the condition that the compression be very nearly adiabatic. Since it was practicable to read the change of volume in less than 30 seconds after the change of pressure had been made, it seemed possible to get very nearly adiabatic compression. This method had the further advantage that, by reading the change of volume rapidly, any drift of temperature, to which we have already referred as a source of error, would be much less serious than if we were obliged to wait for the heat of compression to equalize. To prevent as far as possible any loss of heat during compression, the brass jacket was filled with the same kind of liquid which was in the piezometer. The temperature of the liquid which surrounded the piezometer was therefore raised the same amount by compression as was the temperature of the liquid in the piezometer. There was, of course, some loss due to the heat capacity of the piezometer.

To calculate the heat of compression, we made use of the well-known formula,[8]

$$\Delta t = \frac{1033}{42350} \frac{e}{C_p} T$$

where e is the coefficient of expansion at constant pressure; T is the absolute temperature of the liquid; Δt is the change in the temperature of the liquid due to an adiabatic compression of one atmosphere; and C_p is the specific heat of the liquid at constant pressure. The values of C_p for different temperatures for both ether and alcohol were calculated from the equations given by Regnault,[9]

$$q = 0.529t + 0.000296t^2 \text{ for ether,}$$
$$q = 0.5475t + 0.00112t^2 + 0.00000221t^3 \text{ for alcohol,}$$

where t is temperature of the liquid on the ordinary centigrade scale, and q is the amount of heat in calories required to raise the temperature of the liquid from 0° C. to t° C.

In order, however, to make sure that the method of adiabatic compression would give trustworthy results, the compressibility of alcohol was determined at 20°C. by the first method, — i. e. by waiting for the heat of compression to equalize before the change of volume was read. The compressibility of the same specimen of alcohol was then determined by the second method, in which the change of volume is read rapidly and corrected for the error due to the heat of compression. Ether was examined in a similar way. The values obtained by the first method differing from those obtained by the second method by only one per cent, the method of adiabatic compression was regarded as justified, and was used in all subsequent work on compressibility.

After the piezometer had been filled and had been in the thermostat long enough to assume a constant temperature, observations were made in the way just indicated, on the apparent change of volume of the liquid in glass. The change of volume produced by a change of pressure of 15 cm. of mercury was very small. In such a case, the total movement of the liquid meniscus in the capillary tube amounted to about 0.08 cm., and it was difficult to observe this change of volume accurately. Moreover, the liquid meniscus did not preserve a perfectly symmetrical form, and this caused some error. By taking the mean of twenty observations, — ten made by increasing and ten by decreasing the pressure, — the probable error was reduced to one per cent or less.

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[8] Sir William Thomson, Mathematical and Physical Papers, **3**, 238.

[9] Mém. de l'Acad., **26**, 262 (1862).

Tables IV and V contain the results of these observations on ether and on alcohol. In these tables, *k* is the compressibility when the pressure is expressed in atmospheres, and *P* is the vapor-pressure, in centimeters of mercury, of the liquid at the corresponding temperature *t*.

TABLE IV.

COMPRESSIBILITY OF ETHYL ETHER.

P.	*t*.	Range of Pressure in Cm. of Mercury.	$k \times 10^6$.
46.5	21°.6	152–76	184
		76–47	185
		76–61	184
		61–47	185
56.0	26.5	152–77	195
		152–77	193
		77–56	194
		77–56	193
67.6	31.5	152–77	204
		77–68	206

PART II: LIQUIDS UNDER PRESSURES LESS THAN THEIR VAPOR-PRESSURES.

In order to have a liquid exist under a pressure less than that corresponding to the vapor-pressure at the respective temperature, the gaseous and liquid phases must, of course, not be in contact. In the dilatometer used in the work on the coefficient of expansion described in Part I of this paper, the liquid under investigation was in contact with mercury in such a way that its gaseous phase was not allowed to form. The boundary condition for superheating being thus fulfilled,

TABLE V.

COMPRESSIBILITY OF ETHYL ALCOHOL.

P.	t.	Purity.	Range of Pressure in Cm. of Mercury.	$k \times 10^6$.
4.4	20°.0	% 99.0	150–76	103
			76–56	103
			56–36	103
			36–16	104
			16–6	104
			75–38	103
			40–6	103
4.4	20.1	99.6	154–76	108
			76–56	109
			56–36	109
			56–36	108
			36–16	108
			16–7	108
4.2	19.2	99.5	152–76	106
			76–40	107
			40–6	106
13.3	40.0	99.5	152–76	122
			76–40	122
			40–14	121
32.0	58.3	99.5	153–76	140
			76–36	139

it was at first expected to use this dilatometer for determining the coefficient of expansion and a similar piezometer for determining the coefficient of compressibility in the superheated condition. After some efforts, in which this method was in part successful, it was abandoned for another which has proved more satisfactory.

Apparatus.

The dilatometer used in this part of the work consisted of the cylindrical glass bulb A B, Figure 8, to one end of which was sealed the capillary tube B C D E F, which was bent in the form indicated in that figure. The bulb was about 30 cm. long and 1.7 cm. in diameter and had a capacity of 60.73 $(\text{cm.})^3$. The capillary tube had an internal diameter of about 0.15 cm., except the part from E to F, which had a mean cross section of 0.1506 $(\text{cm.})^2$. In order to keep the temperature constant, the dilatometer was placed in a water-bath, which was heated by means of a Bunsen burner. Since the sides and top of the water-bath were covered with asbestos and the space between the bottom of the water-bath and the table on which it stood was enclosed by asbestos walls, a small flame was sufficient to keep the water-bath at the required temperature. After some attempts it was found possible, by means of an ordinary pinch-cock, to regulate the supply of gas so that the temperature of the water-bath remained sufficiently constant. The capillary tube B C passed out through a rubber stopper in the end of the water-bath, and the U-shaped part C D E F dipped into a large beaker filled with ice and water. For this beaker there was later substituted

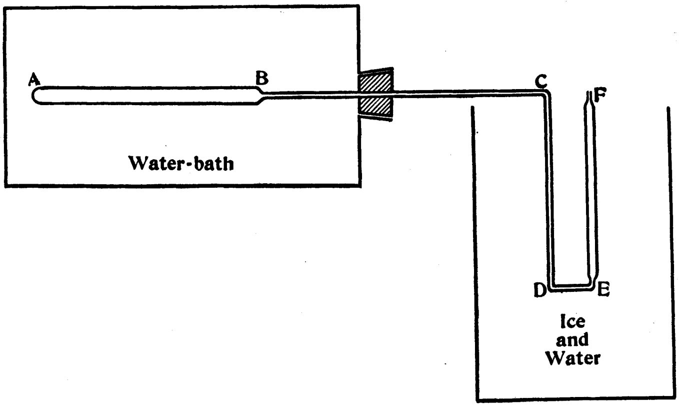

FIGURE 8.

a rectangular brass box with glass windows. In the experiments on the expansion of ether between 0° C. and 16° C. a freezing mixture containing ice, water, and salt, at —2° C., was used instead of ice and water. The liquid in the U-tube was therefore kept near 0° C., while the remainder of the liquid was at a higher temperature. One has here, then, the boundary condition for superheating all the liquid except that contained in the U-shaped part of the capillary tube which dipped into the beaker of ice and water, for it was in contact only with glass or with some of the same sort of liquid at a lower temperature.

The piezometer used in determining the compressibilities in the superheated state was of the same form as the dilatometer. For the vertical tube E F was substituted a smaller tube of cross section 0.0184 $(\text{cm.})^2$. The bulb of the piezometer, which had a capacity of 61.11 $(\text{cm.})^3$, was inserted in a cylindrical brass tube, one end of which was closed with a rubber stopper, through the centre of which passed the capillary tube B C. The other end of this brass tube was closed by means of a disk, in the centre of which was a small tube, through which the interior of the brass tube could be made to communicate with the pressure gauge, so that the pressure on the inside and that on the outside of the bulb of the piezometer were the same. The pressure on the inside of the capillary tube was not equal to that on its outside. On account of this inequality of pressure the internal volume of the capillary tube varied somewhat, and the magnitude of the error introduced into the data on compressibility from this source had to be considered. By means of the formula given on page 117 of Poynting and Thomson's "Properties of Matter," the change in internal volume for a typical case was calculated, and the error introduced from this source was found not to exceed one fifth of one per cent, and may be neglected.

Since in the work on expansion that part of the liquid which was in the U-shaped tube remained at 0° C., it introduced no error into the results. In the work on compressibility, however, the observed change of volume, due to a certain change of pressure on the liquid, was the sum of the change of volume of the liquid in the bulb, which was superheated, and the change of volume of the liquid in the U-shaped tube, which was not superheated, less, of course, the change in the volume of the glass bulb. Knowing the compressibility and the volume of the liquid in the U-shaped tube, one easily made the necessary correction for the error arising from this source, which was about one per cent. There was another correction which had to be applied to the observed change of volume both in compressibility and in expansion. In either of these cases the observed change of volume is supposed to be measured at the temperature of the liquid under investigation. In the present method, however, the change of volume due to a change of temperature or pressure was practically transferred either from the bulb A B (Figure 8), where it had a temperature greater than 0° C., to the tube E F (Figure 8), where its temperature was about 0° C., or from the tube E F back to the bulb A B. In either case it is obvious that the observed change of volume is less than the true change of volume. Taking an approximate value of the coefficient of expansion of the liquid, one at once finds what value the observed change of volume would have if it had been measured at the temperature of the liquid in the bulb instead of at 0° C. The magnitude of this correction varied with the temperature of the liquid in the bulb, but was never greater than seven per cent of the total change of volume.

Expansion.

If observations were to be made on the coefficient of expansion, the dilatometer was filled in the manner already described on page 429 and then placed in position in the water-bath, the temperature of which was raised to the desired value and allowed to become constant. Enough of the liquid was removed from the tube E F (Figure 8) to allow the free surface to stand about 2 cm. above the point E. The end of the tube E F was connected to the pressure gauge described on page 429 and the external pressure on the liquid was made slightly less than the vapor-pressure corresponding to the temperature of the liquid in the bulb of the dilatometer. This temperature was determined by means of a well-tested Baudin thermometer which passed down through the cover of the water-bath and had its bulb near the middle of the cylindrical bulb of the dilatometer. The pressure remaining constant, observations were then made on the change of volume corresponding to a definite change of temperature. Before observing the change of volume a wait of about one hour was allowed for the temperature to attain equilibrium. After observations on the change of volume and on the change of temperature had been made, the external pressure on the liquid was increased, until the liquid was no longer superheated.[10] The liquid was then allowed to cool down to

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[10] This method of procedure was adopted after the first four attempts to obtain values of the coefficient of expansion of ether in the superheated state. In each of these attempts the following peculiarity was noticed.

I had the ether at a temperature of 35° C. and under a pressure of 75 cm. of mercury. Leaving the pressure unchanged, I increased the temperature up to 45° C., and when the temperature had become constant, noted the change of temperature and the corresponding change of volume. Without changing the

TABLE VI.

EXPANSION OF ETHYL ETHER IN THE SUPERHEATED STATE.

P.	p.	t_1.	t_2.	Δt.	$e \times 10^5$.	Mean $e \times 10$.
18.5	18.0	0°	16°.2	16°.2	152	
18.5	17.8	0	19.1	19.1	151	152
43.2	42.0	19.8	34.0	14.2	170	
43.6	42.0	20.2	35.3	15.1	171	
42.0	41.7	19.1	35.8	16.7	170	
42.5	39.2	19.5	35.9	16.4	172	171
64.9	54.1	30.5	40.9	10.4	174	
65.1	51.6	30.6	41.0	10.4	178	
66.3	51.4	31.1	41.2	10.1	177	
64.0	51.9	30.2	41.4	11.2	179	177
80.2	75.0	35.9	44.9	9.0	185	
80.5	75.0	36.1	45.1	9.0	186	
77.9	75.4	35.3	46.9	11.6	184	
77.9	75.4	35.3	45.5	10.2	183	185

pressure, I removed the flame from beneath the water-bath in order to allow the temperature of the ether to return to 35° C., expecting to observe the decrease in volume corresponding to this decrease in temperature. But, instead of cooling quietly down to its former temperature, the ether suddenly changed into vapor shortly after the flame had been removed. It occurred to me that the reversing of the temperature was the cause of this sudden vaporization. I then adopted the method described above, and no further difficulty was encountered from these sudden vaporizations. It is seen that by this method I returned to the unsuperheated state by an increase of pressure instead of by a decrease of temperature.

I do not consider that the four observations which I made justify me in saying that the reversal of the temperature was the true cause of these sudden vaporizations, but as we do not fully understand the conditions of equilibrium of the superheated liquid, it seems best to record these unexplained observations.

its former temperature and a new series of observations commenced. The cross section of the tube E F (Figure 8) being large, no correction was made for the surface film which adhered to its sides.

Tables VI and VII show the results for ethyl ether and ethyl alcohol respectively. In these tables P is the vapor-pressure, in centimeters of mercury, of the liquid at the corresponding temperature t, and p is the external pressure, in centimeters of mercury, on the liquid.

TABLE VII.

Expansion of Ethyl Alcohol in the Superheated State.

P.	p.	t_1.	t_2.	Δt.	$e \times 10^5$.	Mean $e \times 10^5$.
13.3	12.5	40°.3	55°.6	15°.3	119	
13.4	10.3	40.5	55.4	14.9	121	
13.4	10.8	40.6	55.2	14.6	121	
13.4	10.4	40.7	55.1	14.4	120	120
35.8	29.5	60.5	71.1	10.6	132	
35.2	30.2	60.1	70.1	10.0	135	
34.3	27.9	59.5	70.2	10.7	133	
32.0	28.4	58.0	69.3	11.3	131	133

It will be observed from an examination of these tables that the mean of the results obtained under the same conditions has in all cases a probable error of less than one per cent.

Compressibility.

The piezometer, after having been filled, was inserted into the cylindrical brass tube which had been previously filled with water. Both were then placed in position in the water-bath. The connections were made with the pressure-gauge in the usual way. After the temperature of the water-bath had been raised to the desired value and allowed to become constant, it was determined by means of the same Baudin thermometer used in the work on expansion. From an initial value somewhat less than the vapor-pressure of the liquid in the bulb of the piezometer, the pressure was decreased about 40 cm. of mercury and the corresponding change of volume was read. The pressure was then increased to its original value and the change of volume noted. These changes of volume were small and were measured with a cathetometer. The observations were made rapidly, and the apparent change of volume had, therefore, to be corrected for the error due to the heat of compression. This correction was made in the same way in which it was made in Part I of this paper. Here one has, however, to assume that the specific heat of the liquid is about the same in the superheated state as it is when the liquid is not superheated. As it would require a change of ten per cent in the specific heat to produce an error of about one per cent in the compressibility, this assumption seems justified.

TABLE VIII.

COMPRESSIBILITY OF ETHYL ETHER IN THE SUPERHEATED STATE.

P.	*t*.	Range of Pressure in Cm. of Mercury.	$k \times 10^6$.	Mean $k \times 10^6$.
77.4	35°.1	76–27	216	
77.2	35.0	76–27	214	
77.7	35.2	76–27	218	
77.9	35.3	76–27	212	215
88.5	39.1	76–28	226	
88.5	39.1	76–28	225	
88.8	39.2	76–28	224	
89.1	39.3	76–28	224	225

In Tables VIII and IX are given the results for ethyl ether and for ethyl alcohol. Each of the values tabulated in the fourth column of these tables is the mean of twenty observations, ten made by decreasing and ten by increasing the pressure. The mean values in the fifth column have a probable error of about one per cent. In these tables P is the vapor-pressure in centimeters of mercury at the corresponding temperature t. In finding the values of k, pressures are reckoned in atmospheres.

Application to the van der Waals a.

[A considerable part of the following discussion was written by Professor Hall.]

It has already been pointed out that the determination of the coefficients e and k in the neighborhood of the boiling condition was undertaken on account of the importance which is attached to them in the study of the van der Waals a. Professor Hall, in the discussion referred to at the beginning of this paper, dealt with two assumptions relating to the liquid and the vapor conditions :

TABLE IX.

COMPRESSIBILITY OF ETHYL ALCOHOL IN THE SUPERHEATED STATE.

P.	t.	Range of Pressure in Cm. of Mercury.	$k \times 10^6$.	Mean $k \times 10^6$.
75.6	78.0	76–36	158	
75.9	78.2	76–36	156	
75.8	78.1	76–36	156	
76.0	78.3	76–36	157	157

"1, That the pressure due to molecular attraction within a fluid is $\frac{a}{v^2}$, where v is the specific volume and a is some constant;

"2, That the energy per molecule, aside from the potential energy due to the attraction just mentioned, is a function of temperature only, so that it remains constant during any isothermal change of state."

Using the data of Amagat for the expansibility and the compressibility of ethyl ether and ethyl alcohol, he found that, *if assumption* 2 *held good*, [11] assumption 1 could not be true for either of these substances in the liquid state, and that, on the contrary,

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[11] I do not commit myself to the opinion that assumption 2 is necessarily true. It is quite possible that we have in both liquid ether and liquid alcohol some peculiar state of aggregation of the molecules in pairs or triplets or other small groups such as Sutherland has shown the probability of in the case of liquid water. If such groups do not exist in a given liquid, we should, according to the van der Waals hypotheses, expect both assumption 1 and assumption 2 to hold. If such groups do exist in a given liquid, and if their number is independent

"I, a is not a constant but, in each of the liquids examined, a function of both p and T.

"II, In each liquid at constant temperature a increases with increase of volume," that is, with decrease of pressure.

Amagat's data do not, in the case of either liquid, serve for the determination of a with certainty very near the boiling condition at either high or low temperatures. On the other hand Professor Hall, taking the data furnished by Regnault for the evaporation of ether and of alcohol, and taking assumption 2 as holding through the process of vaporization, found by means of a well-known formula the value of a for this process at a number of temperatures in the case of each liquid. The value of a obtained from any set of evaporation data he called a', and the following propositions were established with relation to the values of a and a':

"III, In alcohol a is much less than a' at low temperatures, but with rise of temperature the difference diminishes, a growing larger and a' smaller.

"IV, In ether a, at moderate pressures, is somewhat larger than a'; and both a and a' diminish slowly with rise of temperature, apparently approaching equality."

The formula by means of which a is calculated is

$$a = \left(\frac{e}{k} T - p\right) v^2,$$

in which e = the coefficient of expansion,
k = " " " compressibility,
T = " absolute temperature,
p = " pressure on the liquid,
v = " specific volume of the liquid.

The various quantities entering into this formula are expressed in terms of the c. g. s. system.

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of temperature and pressure, we should expect both assumptions to hold. Perhaps the natural interpretation of the fact that both cannot hold for ether or for alcohol is the hypothesis that such groups do exist in each liquid, but that their number is a function of both temperature and pressure. From this point of view the magnitude of the variations which we find in a, when assumption 2 is held, may be taken as a measure of the discordance of the two assumptions and therefore some indication of the rate of variation of the number of groups with variations of temperature and pressure. It might be better to keep assumption 1, taking a as really constant, and see what change would be necessary in the proposition given as assumption 2.

It appears to be common opinion (see pp. 270 and 271 of the 1904 English edition of Nernst's *Theoretical Chemistry*) that so-called polymerization exists in liquid alcohol but not in liquid ether. E. H. H.

The equation used in finding the values of a' is

$$\rho = a' \left(\frac{1}{v_2} - \frac{1}{v_1} \right),$$

in which, ρ = the internal work of vaporization, in ergs,
v_2 = " specific volume of the liquid state, in cu. cm.,
v_1 = " " " " " saturated vapor " "

The Value of a *in Ether.*

In Table X are given five values of a in ether, calculated by means of my data on compressibility and expansibility. Of these values the first three are for pressures slightly greater than the vapor-pressure, and the last two are at pressures less than the vapor-pressure.

TABLE X.

ETHER.

$t°C.$	$a \times 10^{-7}$.
22°	543
27	541
32	536
36	533
39	537

We have, I believe, no definite information as to the method of purification of the ether used by Amagat. The way in which the ether used by me was purified has already been pointed out. In comparing the values of a obtained from my data with those obtained from the data of Amagat, we must neglect any differences due to difference in purity of the ether used in the two cases. It is doubtful if this would be a source of any considerable error.

For purposes of comparison the values found by Professor Hall for a and a' in ether are given in the following table. The numbers in brackets to the right of each a-column, are, as stated by Professor Hall, "an attempt to establish a regular gradient of a with varying pressure, corresponding in a general way to the indications of the a-column."

TABLE XI.

ETHER.

P (atm.).	20° C. $a' = 495 \times 10^7$.		60° C $a' = 491 \times 10^7$.		100° C. $a' = 482 \times 10^7$.	
	v.	$a \times 10^{-7}$.	v.	$a \times 10^{-7}$.	v.	$a \times 10^{-7}$.
50	1.411	545 (538)	. . .	. . . . . .	. . .	. . . . . .
100	1.400	532 (535)	1.493	515 (527)	1.603	504 (511)
200	1.380	533 (528)	1.462	522 (522)	1.552	506 (508)
300	1.362	509 (521)	1.435	519 (517)	1.514	504 (504)
400	1.347	514 (514)	1.413	518 (512)	1.486	511 (501)
500	1.333	507 (507)	1.393	512 (507)	1.462	503 (498)
600	1.321	504 (500)	1.377	506 (506)	1.439	487 (494)
700	1.309	499 (493)	1.365	501 (497)	1.419	485 (491)
800	1.299	487 (486)	1.352	500 (492)	1.403	485 (488)
900	1.289	475 (497)	1.340	475 (487)	1.387	486 (485)
1000	1.280	472 (473)	1.330	481 (483)	1.374	490 (482)

P (atm.).	138° C. $a' = ?$		198° C. $a' = ?$	
	v.	$a \times 10^{-7}$.	v.	$a \times 10^{-7}$.
50	. . .	. . . . . .	. . .	. . . . . .
100	. . .	. . . . . .	. . .	. . . . . .
200	1.656	510 (509)	. . .	. . . . . .
300	1.600	506 (505)	1.766	491 (500)
400	1.560	502 (501)	1.699	484 (496)
500	1.528	493 (497)	1.648	497 (493)
600	1.500	490 (492)	1.607	506 (490)
700	1.476	484 (488)	1.574	511 (486)
800	1.455	484 (484)	1.545	493 (483)
900	1.435	481 (480)	1.521	465 (480)
1000	1.419	480 (476)	1.500	457 (477)

Examination of Tables X and XI shows that the values of a obtained from my data are in very close accord with those calculated by Professor Hall from the data of Amagat. Indeed, if the bracketed estimates of a given in Table XI were continued by extrapolation to the state of no external pressure, or an external pressure less than one atmosphere, the 20° column would begin with the number 542, as against 543 for 22° in Table X, and the 60° column would begin with the number 532. Interpolation between 542 for 20° and 532 for 60° would give 537 for 40°, whereas Table X gives 537 for 39°. This closeness of agreement is highly satisfactory from one point of view, though it fails to reveal any change of especial interest occurring at or near the point of passage into the superheated condition.

In Professor Hall's paper the values of a' which were calculated from Regnault's evaporation data are not given for temperatures above 100° C. In Table XII below are given a number of values of a' which I have calculated from the probably more accurate evaporation data found by Ramsay and Young.[12] These values are considerably less than the corresponding values obtained from the data of Regnault. This discrepancy is accounted for by the fact that the latent heat of vaporization of ether as given by Ramsay and Young is less than the corresponding value given by Regnault. Now each value of a' given in Table XI is smaller than the value which we have found for a under like conditions of temperature and pressure. The reduction now made in the values of a' by the adoption of Ramsay and Young's data will make the difference between a and a' larger than before. Moreover, a comparison of Table XII with the 198° part of Table XI may seem to indicate that the two values do not approach the same

TABLE XII.

ETHER.

$t°$ C.	$a' \times 10^{-7}$.	$t°$ C.	$a' \times 10^{-7}$.
40°	468	150°	409
60	457	160	398
80	450	170	385
100	434	180	372
110	433	185	362
120	428	190	378
130	422	192	392
140	418	193	395

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[12] Phil. Trans. (1886), p. 123.

limit, as we should expect them to do, near the critical temperature, which is about 194° C. But in explanation it is to be noted that the difference between the bracketed and the unbracketed a-columns is much greater in the 198° part of Table XI than it is elsewhere. Indeed, it now seems quite possible that in the unbracketed a-column at 198° the appearance of a maximum value for a in the neighborhood of 700 atmospheres external pressure is really significant. If the Amagat data enabled us to calculate the value of a at 198° through descending stages of pressure to 50 atmospheres, we might find a rapid fall to a value not very different from that which the Ramsay and Young data give for a' near the critical temperature. On the other hand, Table XII seems to indicate a minimum value of a' near 185° C. with a rise from that point on as the critical temperature is approached; but it is doubtful if the data from which the values of a' have been calculated have sufficient accuracy in the neighborhood of the critical temperature and pressure to allow any importance to be attached to the minimum here suggested.

The Value of a *in Alcohol.*

The values of a given in Table XIII were calculated in the usual way from my data on the compressibility and the expansibility of alcohol. Of these values the first two are for pressures slightly greater than the vapor-pressure, and the last is obtained by using a value of the coefficient of compressibility in the superheated state with a value of the coefficient of expansion in the unsuperheated state. As I have shown that neither of these coefficients is much changed in passing from unsuperheated to superheated state, the above method of getting the value of a at 78° C. causes no serious error.

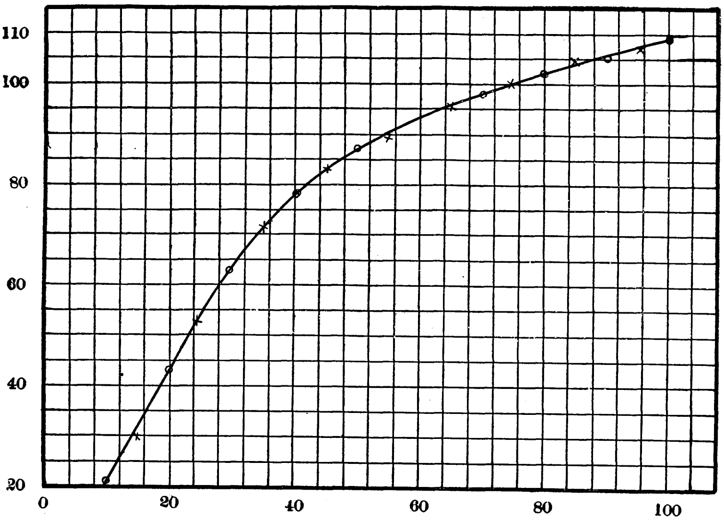
TABLE XIII.

ALCOHOL.

$t.°$ C.	$a \times 10^{-7}$.
20°	481
40	505
78	570

The alcohol examined by me contained 0.5 per cent water. So far as the writer is aware, Amagat does not state the purity of the alcohol which he used, though it is fair to assume that it contained little water.

This lack of information makes it difficult to compare my values of a with those obtained from his data, and it becomes necessary to take up the question of the effect of a small amount of water on the compressibility and on the expansibility of alcohol. The latter part of the problem has been examined by Dupré and Page,[13] and moreover, the necessary information is to be had from tables [14] on the specific gravity of mixtures of alcohol and water. Each of these sources of information indicates that the difference between the coefficients of expansion of absolute alcohol and that of alcohol which contains 0.5 per cent water would not be so much as one per cent of either coefficient and may be neglected here. These facts are brought out clearly by Curve I, in which $e \times 10^6$ is plotted as ordinate and per cent of alcohol as abscissa. The points surrounded by circles are from the data of Dupré and Page and the points marked with crosses are from the tables of densities of mixtures of alcohol and water. It is seen that each set of values gives essentially the same curve; and for points between 99 per cent and 100 per cent alcohol the tangent to the curve makes only a small angle with the axis of abscissae.



CURVE I.

The information heretofore available on the change in compressibility with the presence of water is by no means satisfactory. Pagliani [15] has examined the compressibility of mixtures of alcohol and water, but his mixtures never contained more than 38 per cent of alcohol and his data do not, therefore, throw sufficient light on the question which is here being raised. Dupré and Page have also dealt with this question, but the value for the compressibility of absolute alcohol given by them seems to be in error, as is seen by comparing it with the value given by Röntgen [16] or with that given by Amagat, and this throws doubt on their other data. Moreover, they pass by a single step from 100 per cent to 90 per cent alcohol, and this leaves unexplored the precise region which is of importance here. I have, therefore, examined the compressibility of certain mixtures of alcohol and water with the results given in Table XIV. The last two values, which are of chief importance to this work, completely confirm values obtained earlier in this paper. (See p. 440.) The relation between the compressibility and the per cent of alcohol in these mixtures is brought out in Curve II, in which $k \times 10^6$ is plotted for ordinate and per cent of alcohol for abscissa.

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[13] Phil. Trans. **159**, 591.

[14] Landolt and Börnstein.

[15] Jour. de Phys. (2) **10**, 589 (1891).

TABLE XIV.

COMPRESSIBILITY OF MIXTURES OF ALCOHOL AND WATER.

Per cent of Alcohol by Weight.	Temp. C.°	$k \times 10^6$.
0.0	24°.5	45.9
7.5	24.1	44.1
9.6	25.3	43.2
45.0	25.0	51.8
59.0	23.8	59.8
77.0	22.1	76.0
84.0	24.3	83.0
91.0	24.6	94.0
99.0	24.8	106.0
99.7	23.9	111.0

The points on the curve marked with crosses are from the data of

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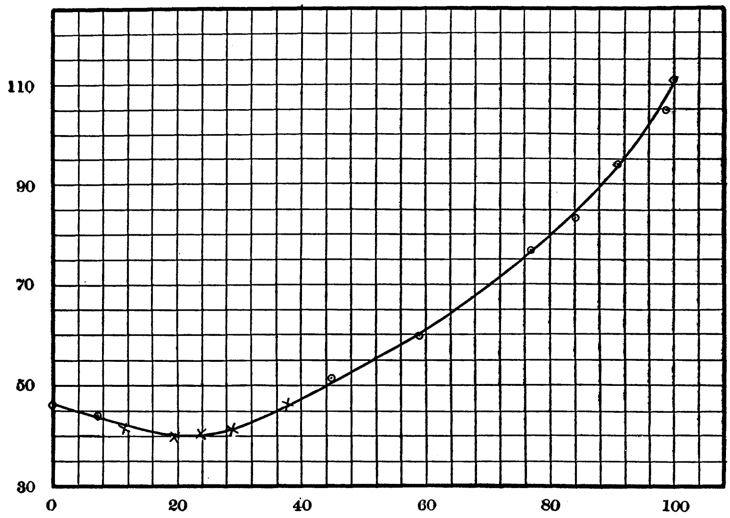
[16] W. A., **44**, 1 (1891).

Pagliani, because my observations did not cover that region. This curve, after passing its well-known minimum, is seen to become steeper as the amount of alcohol in the mixture is increased; and it is seen at once that the compressibility of absolute alcohol decreases rapidly with the introduction of a small amount of water. This decrease in the compressibility would mean an increase in *a*. It is therefore probable that the values of *a* given in Table XIII, which are for alcohol containing 0.5 per cent water, may be as much as 3 per cent greater than the corresponding values for absolute alcohol. Allowing for this possible discrepancy, we may still consider the values here found as being of interest in connection with those obtained from the data of Amagat.



Curve II.

We may perhaps see most clearly the contribution which these recent values make to our knowledge of the van der Waals *a* in alcohol by inserting them in their proper places in the table given by Professor Hall. As given there, they have been corrected for the possible error due to the impurity of the alcohol. That is, I have reduced by 3 per cent the values of *a* given in Table XIII, after making an estimate of the value at 80° from the value at 78°, assuming at the same time that Amagat used absolute alcohol. The values of *a* calculated from my data are enclosed in brackets in order to distinguish them from the values obtained from Amagat's data. The numbers enclosed in parentheses have the same meaning which was attached to the corresponding numbers in the analogous table for ether.

TABLE XV.

ALCOHOL.

P (atm.).	20° C. $a' = 1197 \times 10^7$.		40° C. $a' = 1197 \times 10^7$.		60° C. $a' = 1164 \times 10^7$.	
	v.	$a \times 10^{-7}$.	v.	$a \times 10^{-7}$.	v.	$a \times 10^{-7}$.
		[467]		[490]		
50	1.259	453 (465)	1.285	478 (479)	1.315	483 (496)
100	1.253	458 (463)	1.276	471 (477)	1.306	486 (494)
200	1.242	460 (458)	1.262	476 (472)	1.291	491 (491)
300	1.231	457 (453)	1.250	470 (467)	1.276	494 (487)
400	1.222	449 (448)	1.239	465 (463)	1.265	492 (484)
500	1.214	448 (443)	1.230	459 (459)	1.253	486 (481)
600	1.205	439 (438)	1.222	455 (454)	1.245	479 (477)
700	1.197	422 (433)	1.213	450 (450)	1.236	476 (474)
800	1.189	422 (429)	1.205	444 (446)	1.227	472 (471)
900	1.181	426 (424)	1.197	445 (442)	1.219	464 (468)
1000	1.175	434 (420)	1.189	438 (438)	1.211	466 (465)

P (atm.).	80° C. $a' = 1112 \times 10^7$.		100° C. $a' = 1072 \times 10^7$.	
	v.	$a \times 10^{-7}$.	v.	$a \times 10^{-7}$.
		[556]		
50	. . .	. . . .	. . .	. . . .
100	1.340	531 (533)	1.371	567 (570)
200	1.321	524 (527)	1.350	560 (564)
300	1.306	519 (522)	1.330	556 (559)
400	1.291	521 (517)	1.315	563 (553)
500	1.276	518 (512)	1.300	551 (548)
600	1.265	513 (507)	1.288	538 (542)
700	1.256	506 (502)	1.276	526 (537)
800	1.247	490 (497)	1.268	533 (532)
900	1.239	486 (493)	1.259	521 (527)
1000	1.230	494 (488)	1.250	541 (522)

It will be seen that in the case of alcohol, as in the case of ether, the values of a calculated from the data of this paper are about what one would get by extrapolating from the values previously obtained from the data of Amagat. It is true that the [490] now placed at the head of the 40° column is slightly larger than the numbers beneath it would lead one to expect, and a still greater divergence in the same direction is to be observed at the head of the 80° column. Moreover, these discrepancies would have been considerably greater if a possibly too great allowance (3 per cent) had not been made for the greater impurity of the alcohol used in the research of this paper as compared with the alcohol used by Amagat. But at the most they are hardly great enough to give certain evidence of any noteworthy change in the condition of the alcohol in approaching and passing into the superheated condition.

TABLE XVI.

ALCOHOL.

Temp. C°.	$a' \times 10^{-7}$.	Temp. C°.	$a \times 10^{7}$.
110°	1083	180°	937
120	1069	190	904
130	1050	200	875
140	1035	210	843
150	1019	220	812
160	994	230	769
170	964	240	718

It appears in Table XV that a' decreases and that a increases with rising temperature. Here, as in the case of ether, we find it interesting to follow the change of each of these quantities as far as we can, in order to see how nearly they approach each other in the neighborhood of the critical temperature, which for alcohol is about 243° C. We should of course expect them to approach the same limit in approaching the critical temperature and pressure. The values of a' given in Table XVI were calculated from the evaporation data of alcohol as given by Ramsay and Young. It appears from this table that a' continues to decrease until the critical temperature is approximately reached.

I have made an attempt to obtain values of a at temperatures not very far from the critical temperature. Ramsay and Young have with considerable care plotted some of the high isothermals of alcohol. In obtaining from these curves values of the coefficient of compressibility and of the coefficient of expansion considerable uncertainty was introduced, but at the three temperatures given in the following table it seemed possible to find a value of each of these coefficients having sufficient accuracy to be useful in this paper. The three values of *a* calculated from the coefficients thus obtained are given in Table XVII.

TABLE XVII.

ALCOHOL.

Pressure (atm.).	Temp. C°.	$a \times 10^{-7}$.
67	200°	737
67	210	787
67	220	832

It would appear from Tables XVI and XVII, as they here stand, that the two quantities *a* and *a'* meet and cross in magnitude in the neighborhood of 215° C. This is unlikely. It is more probable that the data for the calculation of *a* and *a'* in the neighborhood of the critical temperature and pressure are somewhat unreliable.

SUMMARY.

1. The coefficient of compressibility, *k*, and the coefficient of expansion, *e*, of ether and of alcohol have been measured at various temperatures at pressures near the saturation pressures of the respective vapors. In some cases the liquids have been examined in the superheated condition. Within the error of my observations these coefficients have been found to be constant over the range of pressure employed in this paper. By reference to Figure 1 the meaning of this result may be more clearly brought out. It states that the slope of any one of the isothermals examined in this paper, — e. g. the isothermal A F H J (Figure 1) — has the same value at C, where the external pressure is somewhat greater than the vapor-pressure, that it has at E, where the external pressure is less than the vapor-pressure; i. e., the direction of the isothermal does not change when the saturation curve is crossed. It has been recently stated by Amagat[17] that nothing is known of the

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[17] Comp. Rend., May 21, 1906.

exact course of the Thomson isothermal where it cuts the saturation curve. It is seen that the present investigation has been able to supply some information on this point.

2. From the data given in Tables II, III, IV, V, VI, and VII, values of the van der Waals a have been calculated, for the two liquids in the various states examined, by the method used by Professor Hall in his paper in the Boltzmann *Festschrift*, that is, by use of the formula $a = \left(\frac{e}{k} T - p\right) v^2$, which assumes, tentatively, that *the energy per molecule, aside from the potential energy due to the attraction* $\frac{a}{v^2}$, *is a function of the temperature only, so that it remains constant during any isothermal change of state.* (But see footnote to p. 447.)

3. The values of a thus found prove in the case of ether to be almost exactly those which would be obtained by extrapolation from the values calculated by Professor Hall from the data of Amagat. There is, therefore, no indication of any significant change of the internal state of ether as it approaches and enters the superheated condition.

A like conclusion is probably to be drawn in the case of alcohol, though the evidence against such a change of internal state upon entering the superheated condition is less satisfactory in the case of alcohol than in the case of ether.

4. From the data of Ramsay and Young on the vaporization of ether the value which Professor Hall calls a' has been calculated for this substance at various temperatures, ranging from 40° C. to 193° C., by means of the formula $a' = \rho \div \left(\frac{1}{v_2} - \frac{1}{v_1}\right)$, in which

ρ = the internal latent heat of vaporization,
v_2 = the specific volume of the liquid state,
v_1 = the specific volume of the saturated vapor state.

These values are smaller than those which Professor Hall found for a' from the Regnault vaporization data for ether, and these latter were smaller than the values found for a at corresponding temperatures. We should expect a and a' to approach the same limit at the critical temperature and pressure. The lack of satisfactory data for determining a in the immediate neighborhood of this condition makes it impossible at present to put this expectation to the proof. The last stage of approach reached in the calculations leaves

$a = 491 \times 10^7$ at 198° C. and 300 atmospheres
$a' = 395 \times 10^7$ at 193° C. and 34.5 atmospheres.

The critical condition is about 194.4° C. and 35.6 atmospheres. There is some indication of a maximum value of a for the temperature 198° C., in the neighborhood of 700 atmospheres.

From the data of Ramsay and Young values of a and of a' have been found for alcohol, supplementary to those calculated by Professor Hall from the data of Amagat and of Regnault. At low temperatures the value of a' in alcohol is more than twice as great as the value of a. At the last stage, at highest temperatures reached in the calculations, the following values were found:

$a = 832 \times 10^7$ at 220° and 67 atmospheres,
$a' = 718 \times 10^7$ at 240° and 60 atmospheres.

The critical condition is about 243° and 63 atmospheres. It would appear, according to the data now available, that the values of a and a' meet and cross in magnitude in the neighborhood of 215° C.; but this seems improbable. Data for the neighborhood of the temperatures here considered are rather dubious.

5. Partly from the data of Pagliani and partly from new data a table (XIV) of the compressibility of mixtures of alcohol and water has been made, ranging from 0 per cent to 99.7 per cent of alcohol. It is found that the effect of a small amount of water is very marked. Thus the compressibility of 99.7 per cent alcohol is about 4 per cent greater than that of 99 per cent alcohol.

6. In four successive attempts to return ether from the superheated state to the unsuperheated state by cooling at constant pressure sudden vaporization occurred, after which this method of procedure was abandoned. No difficulty was experienced in effecting the return by increasing pressure at constant temperature. The reason for the apparent upsetting effect of the cooling process is not evident.

Grateful acknowledgment is made by the writer to Professor Hall for constant advice and personal aid in the course of this work.